

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	1	("6200893").PN.	US-PGPUB; USPAT	OR	OFF	2005/02/22 14:41
L2	6648	(barrier or metal or conductive) and (surface with termination)	US-PGPUB; USPAT	OR	ON	2005/02/22 14:41
L3	3374	(barrier or metal or conductive) and (surface near5 termination)	US-PGPUB; USPAT	OR	ON	2005/02/22 14:42
L4	2183	(barrier or metal or conductive) and (surface near3 termination)	US-PGPUB; USPAT	OR	ON	2005/02/22 14:42
L5	566	4 and (oxidation or oxygen)	US-PGPUB; USPAT	OR	ON	2005/02/22 14:42
L6	442	5 and @ad<"20021029"	US-PGPUB; USPAT	OR	ON	2005/02/22 17:34
L7	83	6 and monolayer	US-PGPUB; USPAT	OR	ON	2005/02/22 17:34
L8	137	(surface near3 (termination or terminating)) and monolayer and barrier	US-PGPUB; USPAT	OR	ON	2005/02/22 17:38
L9	98	8 and @ad<"20021029"	US-PGPUB; USPAT	OR	ON	2005/02/22 17:34
L11	48	9 not 7	US-PGPUB; USPAT	OR	ON	2005/02/22 17:35
L12	2	(surface near3 (termination or terminating)) and monolayer and barrier	USOCR; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2005/02/22 17:38

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	572	(metal with oxide with bridge)	US-PGPUB; USPAT	OR	ON	2005/02/23 09:09
L2	115	(metal with oxide with bridge) and barrier and (metal or conductor or conductive or alloy)	US-PGPUB; USPAT	OR	ON	2005/02/23 09:20
L3	115	(metal with oxide with bridge) and barrier and (metal or conductor or conductive or alloy or conducting)	US-PGPUB; USPAT	OR	ON	2005/02/23 09:10
L4	102	3 and @ad<"20021029"	US-PGPUB; USPAT	OR	ON	2005/02/23 09:10
L5	11	(metal with oxide with bridge) and barrier and (metal or conductor or conductive or alloy)	USOCR; EPO; JPO; DERWENT; IBM_TDB	OR	ON	2005/02/23 09:20

US-PAT-NO: 6727169

DOCUMENT-IDENTIFIER: US 6727169 B1

TITLE: Method of making conformal lining layers for damascene metallization

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Abstract Text - ABTX (1):

Method and structures are provided for conformal lining of dual damascene structures in integrated circuits. Trenches and contact vias are formed in insulating layers. The trenches and vias are exposed to alternating chemistries to form monolayers of a desired lining material. Exemplary process flows include alternately pulsed metal halide and ammonia gases injected into a constant carrier flow. Self-terminated metal layers are thus reacted with nitrogen. Near perfect step coverage allows minimal thickness for a diffusion barrier function, thereby maximizing the volume of a subsequent filling metal for any given trench and via dimensions.

Brief Summary Text - BSTX (2):

The invention relates generally to forming lining layers in high aspect-ratio voids during the fabrication of integrated circuits, and more particularly to barrier layers lining trenches and contact vias in dual damascene metallization schemes.

Brief Summary Text - BSTX (7):

Conductive elements, such as gate electrodes, capacitors, contacts, runners and wiring layers, must each be electrically isolated from one another for proper integrated circuit operation. In addition to providing insulating layers around such conductive elements, care must be taken to prevent diffusion and spiking of conductive materials through the insulating layers, which can cause undesired short circuits between among devices and lines. Protective barriers are often formed between via or trench walls and metals in a substrate assembly, to aid in confining deposited material within the via or trench walls. Barriers are thus useful for damascene and dual damascene interconnect applications, particularly for small, fast-diffusing elements such as copper.

Brief Summary Text - BSTX (8):

Candidate materials for protective barriers should foremost exhibit

effective diffusion barrier properties. Additionally, the materials should demonstrate good adhesion with adjacent materials (e.g., oxide via walls, adhesion layers, etch stop layers and/or metallic materials that fill the vias and trenches). For many applications, a barrier layer is positioned in a current flow path and so must be conductive. Typically, barriers have been formed of metal nitrides (MN.sub.x), such as titanium nitride (TiN), tantalum nitride (TaN), and tungsten nitride (WN), which are dense and adequately conductive for lining contact vias, wiring trenches, and other conductive barrier applications.

Brief Summary Text - BSTX (10):

As illustrated in FIGS. 1 to 2, utilizing a conductive barrier layer and/or other liners makes filling the trenches and vias of dual damascene processing even more difficult. FIG. 1 illustrates a dual damascene process in which an upper insulating layer 10 is formed over a lower insulating layer 12, which is in turn formed over a conductive wiring layer 14, preferably with an intervening dielectric diffusion barrier 15. This dielectric barrier 15 serves to prevent copper or other conductive material of the underlying runner 14 from diffusing into the overlying dielectric layer 12.

Brief Summary Text - BSTX (12):

Protective liners 22, preferably formed of conductive material, are then formed on the exposed horizontal and sidewall surfaces. Typically, the liners 22 at least include a metal nitride, and may additionally include adhesion enhancing and seeding layers. For example, the liner 22 can comprise a tri-layer of Ti/TiN/Cu. In such a structure, the titanium layer serves to improve adhesion with exposed oxide sidewalls; the titanium nitride serves as a diffusion barrier; and a thin copper layer serves as a seed for later electroplating of copper. In other examples, the liners 22 can include tantalum nitride or tungsten nitride barriers.

Brief Summary Text - BSTX (13):

Conformal deposition of the liners 22, however, is very difficult with conventional processing. For example, physical vapor deposition (PVD), such as sputtering, of a metal layer (for adhesion, barrier and/or seed layer) requires at least about 50 .ANG. over all surfaces of the trench 16 and contact via 20. Unfortunately, PVD of metal into high aspect ratio voids necessitates much greater deposition on the top surfaces of the workpiece to produce adequate coverage of the via bottom. For example, typical state-of-the-art trench and contact structures for dual damascene schemes require about 500 .ANG. PVD metal in order for 50 .ANG. of metal to reach the bottom and sidewalls of the contact 20.

Brief Summary Text - BSTX (17):

State-of-the-art CVD processes for depositing barrier layers at temperatures sufficiently low to be compatible with surrounding materials do not operate completely within the surface-controlled regime. Accordingly, even CVD processes, tend to deposit far less material at the bottom of a dual damascene contact 20 than on the upper surfaces and sidewalls of the structure. The upper corners of the trench 16 and the contact 20 represent a high concentration of surface area to volume. Deposition upon the horizontal upper surfaces and adjacent vertical sidewall surfaces merge together to result in an increased deposition rate near the corners 26, 28. Additionally, flowing reactants diffuse slowly into the confined spaces of the trench 16 and contact 20. Accordingly, the concentration of reactants reaching the via bottom 30 is far reduced relative to the concentration of reactants reaching upper surfaces of the structure. Thus, while somewhat improved relative to PVD, CVD step coverage of dual damascene structures remains uneven with most currently known low temperature CVD techniques.

Brief Summary Text - BSTX (22):

In satisfaction of this need, methods are provided herein for depositing lining materials into the high-aspect ratio trenches and contact vias of dual damascene metallization schemes. Advantageously, the methods attain high step coverage, such that only the minimum required thickness of the lining layer need be formed on all surfaces. Examples are provided for applying the methods to formation of one or more of adhesion, barrier and electroplating seed layers.

Brief Summary Text - BSTX (23):

In general, the methods comprise cycles of alternating reactant phases, wherein each phase has a self-limiting effect. "Pure" metal layers, for example, can be formed by alternately adsorbing self-saturating halide- or organic-terminated metal monolayers and reducing the metal-containing monolayer. Metal nitrides suitable for conductive diffusion barriers can be formed by alternately adsorbing self-terminated metal-containing monolayers and conducting ligand exchange reactions, substituting nitrogen-containing species for halogen or organic tails on the metal-containing monolayers. Alternatively, the tails of the self-terminated metal-containing monolayer can be reduced or otherwise removed in an intermediate scavenger or getter phase prior to the nitrogen phase.

Drawing Description Text - DRTX (3):

FIG. 1 is a schematic cross-section of a dual damascene structure having a

conventional **barrier** layer lining the trench and contact via thereof;

Drawing Description Text - DRTX (6):

FIG. 4 is an exemplary gas flow diagram for depositing a **barrier** layer, in accordance with a preferred embodiment of the present invention; and

Detailed Description Text - DETX (5):

With reference to FIGS. 5-8, insulating layers are formed over a semiconductor substrate, in accordance with the preferred embodiments. Referring initially to FIG. 5, first or lower insulating layer 50 is formed over a **barrier** layer 51 and a conductive element 52, which forms part of a lower interconnect layer in the illustrated embodiment. As will be appreciated by the skilled artisan, metallization schemes typically employ one metal composition throughout various wiring layers (e.g., copper interconnects or aluminum interconnects). The preferred embodiments are adaptable to many different materials, but certain embodiments are particularly adapted to lining damascene structures wherein the via floor or lower conductive element 52 comprises a highly conductive copper line. The first insulating layer 50 is preferably formed to a thickness sufficient to insulate the lower conductive element 52 from upper wiring structures to be formed. An etch stop layer or hard mask 54 (FIGS. 6-7) is formed over the lower insulating layer 50 and a second or upper insulating layer 56 (FIG. 8) is formed over the etch stop layer 54. A second etch or CMP stop layer 58 (also known as a shield layer) is preferably also formed over the upper insulating layer 56.

Detailed Description Text - DETX (7):

The etch stop layers 54, 58 of the illustrated embodiment each comprise a material exhibiting different etch rates relative to the insulating layers 50, 56, allowing better control of etching processes. In the illustrated embodiment, the etch stop layers 54, 58 comprise silicon nitride ( $\text{Si.sub.3 N.sub.4}$ ), preferably provided to a thickness of between about 100 .ANG. and 700 .ANG., and more preferably between about 200 .ANG. and 500 .ANG.. The lower **barrier** layer 51 preferably also comprises  $\text{Si.sub.3 N.sub.4}$ .

Detailed Description Text - DETX (14):

Referring now to FIG. 9C, vias that are not fully landed similarly exhibit higher effective aspect ratios. Under such circumstances, the opening 55 of the hard mask 54 overlaps with an edge 70 of the conductive circuit element 52. Small but very high aspect ratio overetch holes 72 are formed in an insulating or dielectric layer 74 surrounding the circuit element 52. The depth of the overetched hole 72 will depend, of course, on the etch selectivity between the **barrier** layer 51 and the surrounding dielectric 74.

Detailed Description Text - DETX (15):

FIG. 9D illustrates the effect of undercutting the barrier layer 51 during via etch. When the barrier 51 is etched by a selective etch from the via bottom to expose the underlying circuit element 52, the barrier 51 tends to be laterally recessed. The resultant cavities 80 are very difficult to line by conventional processes.

Detailed Description Text - DETX (20):

FIG. 3 generally illustrates a method of forming damascene lining layers with high step coverage. The preferred method is a form of atomic layer deposition (ALD), whereby reactants are supplied to the workpiece in alternating pulses in a cycle. Preferably, each cycle forms no more than about one monolayer of lining material by adsorption and preferably by chemisorption. The substrate temperature is kept within a window facilitating chemisorption. In particular, the substrate temperature is maintained at a temperature low enough to maintain intact bonds between adsorbed species and the underlying surface, and to prevent decomposition of the reactant species. On the other hand, the substrate temperature is maintained at a high enough level to avoid condensation of reactants and to provide the activation energy for the desired surface reactions in each phase. Of course, the appropriate temperature window for any given ALD reaction will depend upon the surface termination and reactant species involved.

Detailed Description Text - DETX (23):

If necessary, the exposed surfaces of the dual damascene structure (e.g., the trench and via sidewall surfaces and the metal floor shown in FIG. 9A, or surfaces of a previously deposited adhesion layer) are terminated 102 to react with the first phase of the ALD process. The first phases of the preferred embodiments (see Tables I to IV) are reactive, for example, with hydroxyl (OH) or ammonia (NH<sub>3</sub>) termination. In the examples discussed below, silicon oxide and silicon nitride surfaces of the dual damascene structure do not require a separate termination. Certain metal surfaces, such as at the bottom of the via 61 (FIG. 9A), can be terminated, for example, with ammonia treatment. Where the lining material to be deposited is a metal nitride, surface termination can be considered to include formation of an initial adhesion layer and surface termination thereof, as discussed in more detail with respect to Table I below, possibly with an additional surface termination treatment of the adhesion layer.

Detailed Description Text - DETX (24):

After initial surface termination 102, if necessary, a first chemistry is

then supplied 104 to the workpiece. In accordance with the preferred embodiments, discussed in more detail below with respect to FIG. 4, the first chemistry comprises a metal-containing compound that is reactive with the terminated surfaces left by the previous step 102. Accordingly, a metal-containing species replaces or adsorbs upon the surface termination. This metal-containing species layer is desirably self-terminating, such that any excess constituents of the first chemistry do not further react with the monolayer formed by this process. Preferably a halide or organic ligand terminates the metal-containing monolayer.

#### Detailed Description Text - DETX (28):

In other arrangements, the second chemistry may simply scavenge or remove the ligand termination of the adsorbed metal complex monolayer formed in step 104 (e.g., by ligand-exchange, sublimation or reduction) or otherwise prepare the monolayer for deposition/adsorption of a further monolayer and/or reaction with a further chemistry (see, e.g., Tables I, IV and V below). Desirably, the reaction 108 is also self-limiting. Reactants saturate the limited number of reaction sites left by step 104. Temperature and pressure conditions are preferably arranged to avoid diffusion of reactants from the second chemistry through the monolayer to underlying materials. The second chemistry also leaves a surface termination that operates to limit the deposition in a saturative reaction phase. In the illustrated embodiments of Tables II and III below, nitrogen and  $\text{NH}_3$  terminating a metal nitride monolayer are non-reactive with  $\text{NH}_3$  of the second chemistry.

#### Detailed Description Text - DETX (34):

Depending upon the exposed materials and desired ALD chemistry, an adhesion layer prior to formation of a barrier diffusion may or may not be desired. With TEOS oxides, the inventors have not found the use of an adhesion layer necessary. On the other hand, adhesion layers may be desirable for vias and trenches formed in alternative insulating materials, such as spin-on dielectrics and low k materials. Conductive adhesion layers may also be desirable to facilitate reaction of the first phase over metal runners or landing pads 52 exposed at the bottom of the via 61 (FIG. 9A).

#### Detailed Description Text - DETX (35):

If an adhesion layer is desired, the adhesion layer preferably comprises a "pure" metal lining layer over oxide, metal and etch stop layers of the dual damascene structures. Prior to forming the preferred barrier layers, therefore, a dual damascene structure similar to those of FIGS. 9A to 9E is preferably lined with a metal adhesion layer. As is known in the art, such adhesion layers can be formed by PVD or CVD. For example, PVD titanium and CVD



tungsten processes are well known in the art.

Detailed Description Text - DETX (36):

More preferably, the adhesion layer is formed by ALD, as exemplified by the process recipe of Table I below. It will be understood that the principles disclosed herein with respect to FIG. 3, and with respect to the particular examples of metal nitrides set forth below, are applicable to the formation of a variety of liner materials. For example, a pure metal layer can be deposited by alternately depositing halogen- or organic-terminated monolayers of metal and flowing reduction agents (e.g., H radicals, triethyl boron or other strong reducers) to remove the halogen termination. Removal of the metal monolayer termination by binding and carrying the ligand away can be more generally referred to as "gettering" or "scavenging" the ligand. In the next cycle, therefore, the metal source gas can adsorb upon the underlying metal monolayer in another self-terminating phase. The resultant ALD metal is particularly useful as an adhesion layer prior to **barrier** layer deposition, and as a seed layer following **barrier** deposition and preceding electroplating.

Detailed Description Text - DETX (39):

Methods of Forming Metal Nitride **Barrier** Liners

Detailed Description Text - DETX (40):

FIG. 4 and Tables II to IV below illustrate exemplary processes for forming metal nitride **barrier** layers lining the structures of FIGS. 9A to 9E. For simplicity, like reference numerals are employed to refer to the phases and steps of the metal nitride examples (FIG. 4) that correspond to the general description of FIG. 3.

Detailed Description Text - DETX (42):

Surfaces of the damascene structure upon which the lining material is to be formed are initially terminated to provide a surface that is reactive with the metal source gas. In the embodiment of FIG. 9A, the exposed surfaces upon which deposition is desired include sidewalls of the insulating layers 50, 56 (TEOS in the illustrated embodiment), exposed etch stop layers 54, 58 and the floor of the contact via 62 defined by the lower conductive element 52 (copper in the illustrated embodiment). These surfaces are preferably prepared for **barrier** layer formation by deposition of an adhesion layer, desirably by ALD metal deposition, as discussed above, and a further treatment of the metal adhesion layer with  $\text{NH}_3$ , for example. Without an adhesion layer, reactants of the metal phase 107 can chemisorb upon the oxide and nitride surfaces of the preferred damascene structure without separate **surface termination**. Depending upon the chemistry of the metal phase 107, a surface

treatment of the exposed metal runner 52 can be provided (e.g., with NH.sub.3).

Detailed Description Text - DETX (51):

The cycle 115a is repeated at least about 10 times, and more preferably at least about 20 times, until a sufficiently thick metal nitride is formed to serve a **barrier** function in the dual damascene structure. Advantageously, layers having a thickness of less than about 200 .ANG., and more preferably less than about 100 .ANG., can be formed with near perfect step coverage by the methods of the preferred embodiments.

Detailed Description Text - DETX (53):

The tables below provide exemplary process recipes for forming metal nitride layers suitable for **barrier** applications in dual damascene metallization schemes for ultra large scale integrated processing. Each of the process recipes represents one cycle in a single-wafer process module. In particular, the illustrated parameters were developed for use in the single-wafer ALD module commercially available under the trade name Pulsar 2000.TM., available commercially from ASM Microchemistry Ltd. of Finland.

Detailed Description Text - DETX (56):

Table II above presents parameters for ALD of a titanium nitride (TiN) **barrier** into trenches and contact vias of a dual damascene structure. As noted, the metal source gas comprises titanium tetrachloride (TiCl.sub.4), the carrier gas comprises nitrogen (N.sub.2) and the nitrogen source gas preferably comprises ammonia (NH.sub.3).

Detailed Description Text - DETX (64):

Table IV above presents parameters for another ALD process for forming tungsten nitride (WN). The illustrated embodiment is particularly advantageous for directly depositing a **barrier** layer upon metal at the via floor and insulating surfaces of the trench and via, without an intermediate adhesion layer. As noted, the metal source comprises tungsten hexafluoride (WF.sub.6), the carrier gas comprises nitrogen (N.sub.2) and the nitrogen source gas preferably comprises ammonia (NH.sub.3). In this case, a getter or scavenger removes the ligands left by the metal phase. In particular, a strong reducer, comprising TEB (triethyl boron) in the illustrated embodiment, reduces or otherwise removes the halogen-terminated metal complex monolayer. The nitrogen source gas then readily reacts with the reduced metal surface. In other arrangements, the getter can replace the halogen-termination in a ligand-exchange reaction, desirably leaving a surface reactive with a subsequent nitrogen-containing species. The nitrogen phase saturates the reaction sites left by the getter phase (i.e., the exposed tungsten surface in

the illustrated embodiment) and leaves a nitrogen and NH<sub>3</sub> termination that does not further react with excess ammonia in the saturative phase.

Detailed Description Text - DETX (65):

The intermediate reduction phase results in a metal nitride crystallinity that exhibits lower resistivity than films formed by the ligand-exchange reaction of Table III. Such lowered resistivity is advantageous for the preferred dual damascene **barrier** context, where the **barrier** is placed in the conductive path of integrated circuit wires.

Detailed Description Text - DETX (67):

Once an initial, thin layer (e.g., about 3-10 nm) of metal nitride (e.g., WN) is formed by the method of Table IV, further deposition of **barrier** and/or adhesion materials can proceed without the intermediate scavenger phase. Two phase cycles employing ligand-exchange reactions can more efficiently produce a thicker **barrier** layer over the initial layer. For example, WN by the method of Table IV can be followed by further deposition of TiN, such as by the method of Table II. The upper TiN surface of a WN/TiN **barrier** demonstrates better compatibility with some process flows.

Detailed Description Text - DETX (69):

After formation of the metal nitride **barrier** layer, a seed layer may be desirable, depending upon the method to be employed for filling the dual damascene structure and the conductivity of the deposited **barrier** layer. In the illustrated embodiment, a copper filler is desirably electroplated over the illustrated metal nitride **barriers**. Accordingly, a highly conductive seed layer is preferably first formed over the **barrier** layer.

Detailed Description Text - DETX (70):

As is known in the art, the seed layer preferably comprises a metal layer, more preferably copper, and can be deposited by any of a number of processes. For example, state-of-the-art processing employs PVD or sputtering to form a copper seed layer. In conjunction with high step coverage obtained in forming the prior metal nitride **barrier** layer by ALD, such methods may be adequate for many dual damascene schemes.

Detailed Description Text - DETX (72):

Most preferably, the seed layer is also formed by ALD. The volume saved by high step coverage formation of one or more of the adhesion, **barrier** and seed layers thus contributes to a higher-conductivity line due to a greater volume available for the more conductive filler metal and increased chance of completely filling the contact vias and trenches.

US-PAT-NO: 6638859

DOCUMENT-IDENTIFIER: US 6638859 B2

TITLE: Apparatus and method to achieve continuous interface and ultrathin film during atomic layer deposition

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Detailed Description Text - DETX (5):

However, in a typical situation as noted in the Background section above, the substrate surface does not possess ample bonding sites for all the potential locations on the surface. Accordingly, the ML.sub.x precursor bonding to the surface can result in the formation of islands and grains which are sufficiently far apart to cause the problems noted above. In order to grow continuous interfaces and films, the present invention is practiced to pretreat the surface of the substrate prior to ALD in order to have the surface more susceptible to ALD. In the preferred embodiment the substrate surface is first treated to make the surface more reactive. This is achieved by forming reactive termination on the surface which will then react with the first ALD precursor.

Detailed Description Text - DETX (15):

It is appreciated that the pretreatment of the surface 21 can be achieved to deposit enough radical species to exchange with the surface. In this instance, these radical species (shown as AH in the example illustrated) provide termination sites for bonding to the ML.sub.x precursor. However, in some instances, it may be desirable to actually deposit an intermediate layer above the surface 21. In this instance, an actual intermediate layer 23 is formed above the surface 21 and in which the termination sites are actually present on this layer 23. This is illustrated in FIG. 10. Again, this layer can be deposited by a plasma process, including ALD. Then, the ALD process sequence, commencing with the deposition of ML.sub.x can commence.

Detailed Description Text - DETX (18):

It is appreciated that the pretreatment of surface 21 is achieved by a plasma process in the above description, including the use of ALD. However, other techniques can be used instead of a plasma process to pretreat the surface 21. Thus, the surface 21 can be treated, even the intermediate layer 23 grown, by other techniques. Furthermore, a leaching process can be utilized. Since some surfaces are quite inert, a process other than reactive exchange or attachment may be desirable. For example, hydrocarbon and fluorocarbon polymers are utilized for low-k dielectrics. Adhesion of films, for sealing (insulating) or for forming a barrier (metals, metal nitrides), is difficult to achieve. In these instances, leaching hydrogen or fluorine from the top layer of the polymer can activate the surface for ALD.

Claims Text - CLTX (1):

1. A method to perform atomic layer deposition comprising: pretreating a surface of a substrate or a material layer formed on the substrate by introducing a radical specie including any combination of O.sub.2, H.sub.2, H.sub.2 O, NH.sub.3, NF.sub.3, N.sub.2, Cl and F to increase AHx termination sites on the surface, where x is an integer and A is a non-metal capable of bonding with hydrogen H; introducing a first precursor to deposit a first reactive specie on the surface, the surface when pretreated being more receptive to have additional bonding with the first reactive specie, due to the increase of AHx termination sites on the surface; and introducing a second precursor, after the bonding of the first reactive specie, to deposit a second reactive specie to react with the deposited first reactive specie to form a film layer.

Claims Text - CLTX (4):

4. The method of claim 1 wherein said pretreating the surface forms NHx termination sites.

Claims Text - CLTX (12):

12. The method of claim 7 wherein Al.sub.2 O.sub.3 is deposited on Ti by atomic layer deposition in which said pretreating includes introducing NH.sub.3 /H.sub.2 /N.sub.2 plasma to nitridize the surface to form NH.sub.x as the termination sites on Ti.

Claims Text - CLTX (13):

13. The method of claim 7 wherein Al.sub.2 O.sub.3 is deposited on W by atomic layer deposition in which said pretreating includes introducing NH.sub.3 /H.sub.2 /N.sub.2 plasma to nitridize the surface to form NH.sub.x as the termination sites on W.

Claims Text - CLTX (14):

14. The method of claim 7 wherein Al.sub.2 O.sub.3 is deposited on Ta by atomic layer deposition in which said pretreating includes introducing NH.sub.3 /H.sub.2 /N.sub.2 plasma to nitridize the surface to form NH.sub.x as the termination sites on Ta.

Claims Text - CLTX (30):

30. A method to perform atomic layer deposition comprising: depositing an intermediate layer; pretreating a surface of the deposited intermediate layer by introducing a radical specie including any combination of O.sub.2, H.sub.2, H.sub.2 O, NH.sub.3, NF.sub.3, N.sub.2, Cl and F to increase AHx termination sites on the surface, where x is an integer and A is a non-metal capable of bonding with hydrogen H; introducing a first precursor to deposit a first reactive specie on the surface, the surface when pretreated being more receptive to have additional bonding with the first reactive specie, due to the increase of AHx termination sites on the surface; and introducing a second precursor, after the bonding of the first reactive specie, to deposit a second reactive specie to react with the deposited first reactive specie to form a film layer.

Claims Text - CLTX (31):

31. A method to perform atomic layer deposition comprising: leaching hydrogen or fluorine from a surface by pretreating the surface by introducing a radical specie including any combination of O.sub.2, H.sub.2, H.sub.2 O, NH.sub.3, NF.sub.3, N.sub.2, Cl and F to increase AHx **termination sites on the surface**, where x is an integer and A is a non-metal capable of bonding with hydrogen H; introducing a first precursor to deposit a first reactive specie on the surface, the surface when pretreated being more receptive to have additional bonding with the first reactive specie, due to the increase of AHx **termination sites on the surface**; and introducing a second precursor, after the bonding of the first reactive specie, to deposit a second reactive specie to react with the deposited first reactive specie to form a film layer.